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May 1995



**DIRECT EXPOSURE PROBE/MASS
SPECTROMETRY AND PYROLYSIS-GAS
CHROMATOGRAPHY/MASS SPECTROMETRY
STUDY OF THE EFFECT OF GAMMA RADIATION
EXPOSURE ON THE THERMAL DEGRADATION
PRODUCTS OF NATURAL RUBBER
— POLYCAPROLACTONE MIXTURES —**

John A. Hiltz — Terry Foster

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Approved by H.M. Merklinger
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ABSTRACT

This report describes the results of direct exposure probe-mass spectrometry and pyrolysis-gas chromatography/mass spectrometry studies of the effect of gamma radiation exposure on the thermal degradation products of natural rubber, polycaprolactone, 70 - 30 and 30 - 70 mixtures of natural rubber and polycaprolactone. The degradation products and their relative abundances of the natural rubber, polycaprolactone, and the 70 - 30 natural rubber - polycaprolactone mixture were similar before and after gamma radiation exposure. However, gamma radiation exposure did have an effect on the degradation products of the 30 - 70- natural rubber - polycaprolactone mixture. Prior to gamma radiation exposure, the degradation products of this mixture consisted of compounds characteristic of the two components of the mixture, while following gamma radiation exposure the degradation products were characteristic of the polycaprolactone portion of the mixture. Degradation products from the natural rubber portion of the mixture were not observed. Although this suggests that gamma radiation exposure changed the structure of the mixture, other techniques, such as sol gel analysis or molecular weight determination, are required to determine how the structure has changed.

RÉSUMÉ

Dans ce rapport, on décrit les résultats d'études sur l'effet d'une exposition aux rayons gamma sur les produits de dégradation thermique du caoutchouc naturel, de la polycaprolactone et de mélanges à 70/30 et à 30/70 de caoutchouc naturel et de polycaprolactone; ces études ont été effectuées par spectrométrie de masse à sonde d'exposition directe et par spectrométrie de masse/chromatographie des gaz de pyrolyse. Les produits de dégradation thermique du caoutchouc naturel, de la polycaprolactone et du mélange à 70/30 de caoutchouc naturel et de polycaprolactone, ainsi que leurs abondances relatives étaient semblables avant et après l'exposition aux rayons gamma. Toutefois, l'exposition aux rayons gamma modifiait les produits de dégradation du mélange à 30/70 de caoutchouc naturel et de polycaprolactone. Avant l'exposition aux rayons gamma, les produits de dégradation de ce mélange étaient constitués de composés caractéristiques des deux constituants; par contre, après l'exposition, les produits de dégradation étaient caractéristiques de la polycaprolactone. La présence de produits de dégradation du caoutchouc naturel n'a pas été décelée. Ces résultats laissent supposer que l'exposition aux rayons gamma modifie la structure du mélange; néanmoins, il faudra faire appel à d'autres techniques, comme l'analyse sol-gel ou la mesure du poids moléculaire, pour déterminer de quelle façon cette structure a été modifiée.

Executive Summary

DREA Technical Memorandum

"Direct Exposure probe/Mass Spectrometry and Pyrolysis-Gas Chromatography/Mass Spectrometry Study of the Effect of Gamma Radiation Exposure on the Thermal Degradation Products of Natural Rubber - Polycaprolactone Mixtures", John A. Hiltz and Terry Foster.

Concern for the accumulation of plastic waste has led to a search for polymeric materials that will degrade rapidly when exposed to the environment. One polymeric material that is rapidly degraded is polycaprolactone (PCL). The structure of this polymer is such that it is very susceptible to hydrolysis of the ester linkages in the polymer chain.

DREP (Dr. Terry Foster) has investigated PCL/natural rubber (NR) blends as degradable materials for use as garbage bags on CF ships. One problem with these materials was poor mechanical properties. Gamma irradiation of the blends was tried to determine if this would improve the mechanical properties of the blends. As part of this study, DREA (Dr. John Hiltz) was asked to study the effect of gamma radiation exposure on the structure of some PCL/NR blends using direct exposure probe/mass spectrometry (DEP/MS) and pyrolysis gas chromatography/mass spectrometry (py-GC/MS). In particular, there was interest in whether or not a technique such as DEP/MS was sensitive to any changes in the structure of the blends following gamma radiation exposure.

This TM summarizes the results of the DEP/MS and py-GC/MS analysis of the effect of gamma radiation on the degradation products of NR, PCL, a 70/30 NR/PCL blend, and a 30/70 PCL/NR blend. Gamma radiation exposure had little effect on the degradation products released from the NR, PCL, or 70/30 NR/PCL blend following DEP or pyrolytic heating. However, gamma radiation exposure led to a marked difference in the degradation products of the 30/70 NR/PCL blend. This is consistent with gamma radiation exposure leading to increased cross-linking in the NR portion of the blend or to increased interaction between the two components of the blend. These results are consistent with the results of mechanical tests that showed that gamma irradiation led to higher tensile strengths and less elongation for the blend samples.

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1.0 Introduction

Thermal degradation coupled with techniques that separate, detect, and identify degradation products provides a powerful means of analyzing intractable materials such as thermoset polymers and cross-linked elastomers. The successful application of techniques such as pyrolysis gas chromatography (py-GC)¹⁻⁷, py-GC/mass spectrometry (MS) and direct exposure probe (DEP)/MS⁸⁻¹⁶ to the study of polymeric materials requires an understanding of the relationship between polymer structure and polymer degradation mechanisms. If the degradation mechanism of a particular polymer is known, then the polymeric material can be identified on the basis of its characteristic degradation products. Conversely, if the structure of the material is known, then identification of degradation products can be used to elucidate degradation pathways.

The identification of a polymeric material on the basis of its thermal degradation products can be complicated by several factors. These include the presence of fillers, processing aids, extenders, and plasticizers in the polymer; the degree of cross-linking of the polymer; and whether or not the polymer has been blended with another polymer. Additives, such as plasticizers and extenders, can often be identified in the degradation products of the polymer following pyrolysis. Alternatively, extenders and plasticizers can be leached from the polymer and identified. Although cross-linking of a polymeric material may be evident from a change in the degradation products of a polymer, cross-linking is usually assessed with mechanical tests, techniques such as dynamic mechanical thermal analysis, and chemical methods such as sol-gel analysis. The effect of blending on the degradation products will depend on the nature and compatibility of the polymers in the blend.

In this paper, the results of py-GC/MS and DEP/MS analysis of several polymers, before and after exposure to gamma radiation, are reported. The aim of this study was to determine if py-GC/MS and/or DEP/MS could be used to monitor changes in these polymers that might result from exposure to gamma radiation. That is, could changes in the structure of the polymers, such as radiation induced cross-linking or bond cleavage, be correlated with changes in the relative amounts or the nature of the degradation products released from the samples. Further, if differences in degradation products released from the polymers before and after gamma radiation exposure were observed, the changes would be discussed in relationship to changes in structure induced by exposure to gamma radiation.

2.0 Experimental Approach

2.1 Materials

Samples of natural rubber (polyisoprene), polycaprolactone, and two mixtures of natural rubber and polycaprolactone, referred to as Mixture A and Mixture F, were used in this study. Mixture A contained 70% natural rubber and 30% polycaprolactone while Mixture F contained 30% natural rubber and 70% polycaprolactone. The materials were analyzed before and after exposure to gamma radiation.

2.2 Equipment

A CDS direct exposure probe (DEP) (Chemical Data Systems, Oxford, Pennsylvania) was used for all DEP analysis. The DEP filament current was programmed to increase from 0 to 610 milliamps (mA) at a rate of 20 mA/s. The manufacturer's literature indicated that each milliamp increase in current to the filament corresponded to a 1°C increase in temperature. Therefore, the heating rate was approximately 20°C/s and the final temperature of the filament was approximately 610°C. Samples were either dissolved in toluene or ground in toluene prior to application to the probe filament. The toluene was allowed to evaporate prior to heating of the filament.

Mass spectra were acquired on a quadrupole mass spectrometer (Finnigan MAT model 5100) at 70 electron volts (eV) in the full scan mode from 20 to 360 atomic mass units (amu) in 0.24 seconds. The centroid sampling interval was 2 ms.

A CDS Model 170 Pyrolysis Unit (Chemical Data Systems, Oxford Pennsylvania) with a platinum coil filament was used for all pyrolysis. Typically, 0.5 mg of sample was pyrolyzed in a 25 mm quartz pyrolysis tube using a heating rate of 0.1°C/ms to a final temperature of 610°C. The pyrolysis products were separated on a 30 m long X 0.25 mm inside diameter 5% phenyl - 95% methyl silicone (DB-5, J&W Scientific) 0.25µm thick bonded phase capillary column using helium as the carrier gas. The carrier gas flow rate was approximately 1.0 mL/min at 40°C. The GC oven was temperature programmed from 40°C (hold time 4 minutes) to 300°C at a rate of 10°C/min and finally held at 300°C for 10 minutes.

Mass spectra of the separated pyrolysis products were acquired on a quadrupole mass spectrometer (Finnigan MAT 5100 GC/MS) in the full scan mode (30 to 500 amu) using a 2 second scan time and a 10 ms centroid sampling interval.

3.0 Results

The mass spectrum of a compound following DEP analysis results from the fragmentation of the degradation products formed during the heating of the sample by the direct exposure probe. That is, the mass spectrum is a composite of the mass spectra of the various degradation products formed during the analysis. Therefore discussion of differences in the mass spectra of compounds following DEP analysis must take into consideration factors that would affect the degradation mechanisms and therefore the thermal degradation products of those compounds.

Py-GC/MS analysis of the samples was done in conjunction with DEP analysis. GC separation of the thermal degradation products of samples prior to MS analysis allowed identification of the degradation products. Knowledge of the major degradation products was used to explain the major ions in the DEP reconstructed ion chromatogram (RIC).

3.1 Direct Exposure Probe/Mass Spectrometry (DEP/MS) and Pyrolysis-Gas Chromatography/Mass Spectrometry (py-GC/MS) Analysis

3.1.1 Natural Rubber

3.1.1.1 Py-GC/MS

The reconstructed ion chromatograms (RICs) of samples of natural rubber and gamma radiation exposed natural rubber following pyrolysis at 610°C are shown in Figures 1a and 1b respectively. Comparison of the RICs indicated that the degradation products produced by the pyrolysis of the natural rubber and the natural rubber sample exposed to gamma radiation were similar. Mass spectral analysis indicated that the major peak in the pyrograms of the samples was 1-methyl-4-(1-methylethenyl)cyclohexene ($C_{10}H_{16}$) (scan 294 - Figure 1a and scan 295 - Figure 1b). 1-methyl-4-(1-methylethenyl)cyclohexene is the dimer of the monomeric unit of natural rubber (2-methyl-1,3-butadiene, C_5H_8). Compounds with molecular weights corresponding to the trimer ($C_{15}H_{24}$), tetramer ($C_{20}H_{32}$), pentamer ($C_{25}H_{40}$) and hexamer ($C_{30}H_{48}$) of 2-methyl-1,3-butadiene were found in the groupings of peaks centered at scan 500, scan 675, scan 780,

and scan 880 respectively in both pyrograms. Other degradation products included structural isomers of the dimer, trimer, tetramer, pentamer and hexamer, that is, compounds containing 10, 15, 20, 25 and 30 carbon atoms, and aromatics, such as 1-methyl-4-(1-methylethenyl)benzene, that are formed by dehydrogenation of the major degradation products.

The thermal degradation pathways of natural rubber leading to the major degradation products, such as 2-methyl-1,3-butadiene (C_5H_8), the dimer ($C_{10}H_{16}$), trimer ($C_{15}H_{24}$), and tetramer ($C_{20}H_{32}$) of 2-methyl-1,3-butadiene, are shown in Scheme 1.

3.1.1.2 DEP Analysis

The reconstructed ion chromatograms (RICs) of samples of natural rubber and gamma radiation exposed natural rubber following DEP analysis at $610^\circ C$ are shown in Figures 2a and 2b respectively. Both RICs have one major peak. The mass spectra of the major peak in each of the RICs (scan 137 and scan 131 respectively) are shown in Figures 3a and 3b, while the most intense ions and their relative abundances for the natural rubber samples before and after gamma radiation exposure are listed in Table 1.

TABLE 1

The m/z and relative abundances of fragments produced by the Direct Exposure Probe (DEP) analysis of natural rubber and gamma radiation exposed natural rubber.

Natural Rubber		Gamma Radiation Exposed Natural Rubber	
m/z	Relative Abundance	m/z	Relative Abundance
68	100.0	68	100.0
93	46.5	93	52.7
80	31.9	53	38.3
53	29.4	80	28.5
40	22.3	40	28.5
39	15.5	121	16.1
121	15.3	39	15.0
107	8.1	42	12.4
42	7.5	136	8.8
136	7.5	107	8.7

The most intense ion in the mass spectra of the samples of natural rubber had a mass of 68 (m/z 68) which corresponds to an ion with a molecular formula C_5H_8 . This could arise from 2-methyl-1,3-butadiene, the monomeric unit of natural rubber, or from the

fragmentation of the dimer, trimer and tetramer of 2-methyl-1,3-butadiene. The ions at m/z 53 (C_4H_5) and m/z 40 (C_3H_4) are formed from the fragmentation of the monomer, dimer, trimer, and higher molecular weight oligomers. The ions at m/z 136 ($C_{10}H_{16}$), m/z 204 ($C_{15}H_{24}$) and m/z 272 ($C_{20}H_{32}$) are the molecular ions of the dimer, trimer, and tetramer of 2-methyl-1,3-butadiene respectively. These ions can also be formed from the fragmentation of higher molecular weight degradation products. For instance, the ion at m/e 136 could be formed from the trimer ($C_{15}H_{24}$) following the loss of the radical C_5H_8 . Loss of a methyl group (CH_3) from the dimer ($C_{10}H_{16}$) gives rise to the ion at m/z 121, while the loss of a C_3H_7 gives rise to the ion at m/z 93, and the loss of C_4H_8 gives rise to the ion at m/z 80.

The mass spectral fragmentation pathways that give rise to the major ions in the DEP/MS RIC of natural rubber are shown in Scheme 2.

Comparison of the mass spectra produced by the DEP analysis of natural rubber samples before and after exposure to gamma radiation indicated that there was little difference in the mass spectra produced by the two samples. That is, the ions and the relative abundances of the ions, produced following DEP analysis of the natural rubber and gamma radiation exposed natural rubber, were similar.

3.1.2 Polycaprolactone

3.1.2.1 Pyrolysis

The RICs of samples of polycaprolactone and gamma radiation exposed polycaprolactone following py-GC/MS analysis at 610°C are shown in Figures 4a and 4b respectively. Mass spectral analysis indicated that the major degradation products of the PCL samples before and after gamma radiation exposure were caprolactone (scan 365 and scan 363 respectively), and compounds containing 2, 3, and 4 ring opened caprolactone units (scans 610, 844 and 1086 for the PCL sample and scans 615, 843 and 1085 for the gamma radiation exposed PCL sample). Further, the relative quantities of these degradation products were similar for the PCL samples before and after gamma radiation exposure.

The thermal degradation pathways of polycaprolactone are shown in Scheme 3. Major thermal degradation products include caprolactone (oxepanone), hexenoic acid, hexanoic acid, and products that contain 2, 3 and 4 chain opened caprolactone units.

3.1.2.2 DEP Analysis

The mass spectra of samples of PCL and gamma radiation exposed PCL following DEP analysis at 610°C are shown in Figures 5a and 5b. The most intense ions in the mass spectra of the samples and the relative abundances of the ions are listed in Table 2.

TABLE 2

The m/z and relative abundances of fragments produced by the Direct Exposure Probe (DEP) analysis of samples of uncross-linked and gamma radiation cross-linked samples of polycaprolactone (PCL).

Polycaprolactone		Gamma Radiation Exposed Polycaprolactone	
m/z	Relative Abundance	m/z	Relative Abundance
55	100.0	55	100.0
42	50.9	42	70.8
115	30.8	115	43.7
69	28.5	69	36.5
84	22.7	84	27.2
39	17.1	97	16.7
97	13.4	39	9.8
73	3.8	73	6.4
211	0.7	211	1.2
229	0.4	229	0.6

The most abundant ions are at m/z 55 and m/z 42, which correspond to the molecular fragments C_4H_7 and C_3H_6 respectively. These arise from the fragmentation of caprolactone and thermal degradation products containing 2, 3, and 4 ring opened caprolactone monomers. The ion at m/z 115 ($C_6H_{11}O_2$) results from the fragmentation of dimers, trimers, tetramers, etc., released during the thermal degradation of the polymer. The ion at m/z 69 corresponds to the fragment C_5H_9 and is formed from the fragmentation of caprolactone or the degradation products containing 2 or more ring opened caprolactone units. The ion at m/z 97 arises from the acyl oxygen cleavage of the dimer, trimer, and higher molecular weight oligomers. The loss of CH_2O from caprolactone gives rise to the ion at m/e 84. The ion at m/z 229 can arise from the degradation product containing 2 caprolactone units or from the fragmentation of the thermal degradation products containing 3 or more ring opened caprolactone units. The ion at m/z 211 results from the loss of the $C_6H_{11}O_3$ radical from the trimer (MW 342).

The mass spectral fragmentation of several of the thermal degradation products of polycaprolactone are shown in Scheme 4.

As was observed for natural rubber, the ions and their relative intensities produced by the thermal degradation of the PCL before and after gamma radiation exposure were very similar.

3.1.3 Mixture A (70% natural rubber - 30% polycaprolactone)

3.1.3.1 Pyrolysis

The RICs of samples of mixture A and gamma radiation exposed mixture A following py-GC/MS analysis at 610°C are shown in Figures 6a and 6b respectively. Comparison of the major peaks in the RIC of mixture A with the major peaks in the RICs of PCL and natural rubber indicates that the thermal degradation of mixture A releases products that are characteristic of the constituents of the mixture, that is, natural rubber and PCL. For instance, in the pyrogram of mixture A, the peak at scan 296 and the groupings of peaks centered at scans 500, 675, 780, and 880 are characteristic of the pyrolytic degradation of natural rubber. The peaks at scans 365, 617, 845, and 1099 are characteristic of the pyrolytic degradation of polycaprolactone. The pyrogram of the gamma radiation exposed mixture A had the same peaks as were found in mixture A. Further, there was little difference in the relative amounts of degradation products released by mixture A before and after gamma radiation exposure.

3.1.3.2 DEP Analysis

The mass spectra of samples of mixture A and gamma radiation exposed mixture A following DEP analysis at 610°C are shown in Figures 7a and 7b respectively. The most intense ions in the mass spectra of the samples and their relative abundances are listed in Table 3.

There was little difference in the mass spectra from the two samples. That is, both the masses and the relative intensities of the ions produced from the degradation of the samples of mixture A and gamma radiation exposed mixture A were similar. Ions at m/z 204, m/z 136, m/z 121, m/z 107, m/z 93, m/z 80, m/z 69, m/z 53 and m/z 42, which are characteristic of the degradation of natural rubber, and ions at m/z 229, m/z 115, m/z 97, m/z 84, m/z 55, m/z 42, and m/z 39, which are characteristic of the degradation of

polycaprolactone, were found in the mass spectra of both samples. However, unlike the polycaprolactone samples, neither of the mixture A samples had an ion at m/z 69.

TABLE 3

The m/z and relative abundances of fragments produced by the Direct Exposure Probe (DEP) analysis of samples of Mixture A (70% natural rubber - 30% PCL) before and after gamma radiation exposure.

Uncross-linked		Cross-linked	
m/z	Relative Abundance	m/z	Relative Abundance
68	100.0	68	100.0
94	33.3	94	36.3
42	30.7	42	30.4
53	27.8	80	29.9
80	25.8	53	28.6
39	19.8	39	20.0
121	15.2	55	17.1
107	11.1	121	16.9
55	9.8	107	9.6
136	8.1	136	8.9
84	6.4	115	6.2
115	6.0	84	5.9
97	3.7	97	4.1

3.1.4 Mixture F (30% natural rubber - 70% polycaprolactone)

3.1.4.1 Pyrolysis

The RICs of samples of mixture F and gamma radiation exposed mixture F following py-GC/MS analysis at 610°C are shown in Figures 8a and 8b respectively. Comparison of the RICs for the samples of mixture F and gamma radiation exposed mixture F indicates that the nature of the degradation products of changed following gamma radiation exposure. That is, the degradation products produced by the gamma radiation exposed sample of mixture F were characteristic of the PCL component of the mixture. Degradation products characteristic of the natural rubber portion of the mixture were absent in the pyrogram. This is in contrast to the degradation products produced by mixture F prior to radiation exposure that were characteristic of both the PCL and natural rubber components of the mixture.

3.1.4.2 DEP Analysis

The mass spectra of mixture F and gamma radiation exposed mixture F following DEP analysis are shown in Figures 9a and 9b respectively. The most intense ions in the mass spectra and their relative abundances are listed in Table 4. Gamma radiation exposure resulted in a change in the ions produced following DEP analysis of Mixture F. For instance, mixture F produced ions at m/z 136, m/z 121, m/z 93, m/z 80, and m/z 68 that are characteristic of natural rubber and ions at m/z 115, m/z 97, m/z 84, and m/z 42 that are characteristic of polycaprolactone. However, the mass spectrum of mixture F following gamma radiation exposure did not have the ions at m/z 136, m/z 121, m/z 93, m/z 80 and m/z 68 associated with the natural rubber portion of the mixture, but did have the ions at m/z 115, m/z 97, m/z 84, m/z 69, m/z 55 and m/z 42, which are characteristic of the degradation of polycaprolactone.

The lack of ions released from the degradation of the natural rubber portion of the mixture is indicative of a change in the sample of mixture F exposed to gamma radiation.

TABLE 4

The m/z and relative abundances of fragments produced by the Direct Exposure Probe (DEP) analysis of samples of uncross-linked and gamma radiation cross-linked samples of Mixture F (30% natural rubber - 70% PCL).

Uncross-linked		Cross-linked	
m/z	Relative Abundance	m/z	Relative Abundance
42	100.0	55	100.0
68	94.8	42	86.0
39	73.7	69	29.5
54	73.4	84	23.8
93	54.3	115	22.4
79	53.7	39	8.5
115	30.3	97	7.0
121	25.6	73	4.5
51	20.4	80	2.6
108	17.3		
97	16.3		
84	9.2		
136	8.6		

4.0 Conclusions

DEP GC/MS and py-GC/MS analyses could not be used to differentiate between samples of natural rubber before and after gamma radiation, samples of polycaprolactone before and after gamma radiation, or samples of a 70% natural rubber - 30% polycaprolactone (mixture A) before and after gamma radiation exposure. That is, the degradation products and their relative amounts before and after gamma radiation exposure were similar. However, it cannot be concluded that changes in the structure of the materials had not taken place, only that any change that might have taken place had very little effect on the degradation pathways of these three samples.

In contrast to the other three samples, the degradation products of mixture F (30% natural rubber - 70% polycaprolactone) changed considerably following gamma radiation exposure. Specifically, the degradation products characteristic of the natural rubber portion of the sample were reduced substantially relative to the degradation products characteristic of the polycaprolactone portion of the sample following gamma radiation exposure. This suggests that gamma radiation exposure led to changes in the structure of this material. This could result from an increase in the cross-linking in the natural rubber portion of the mixture or from an increase in the interaction between the natural rubber and polycaprolactone portions of the mixture. These results are consistent with the results of mechanical tests on these samples that showed that gamma radiation exposure led to higher tensile strengths and less elongation for the blend samples.

To fully understand how gamma radiation exposure led to a change in the pyrolytic degradation products of mixture F requires further analysis of this polymer before and after gamma radiation exposure. This could involve the use of sol gel analysis to determine the degree of cross-linking or HPLC to determine if the molecular weight of the material had changed considerably following gamma radiation exposure.

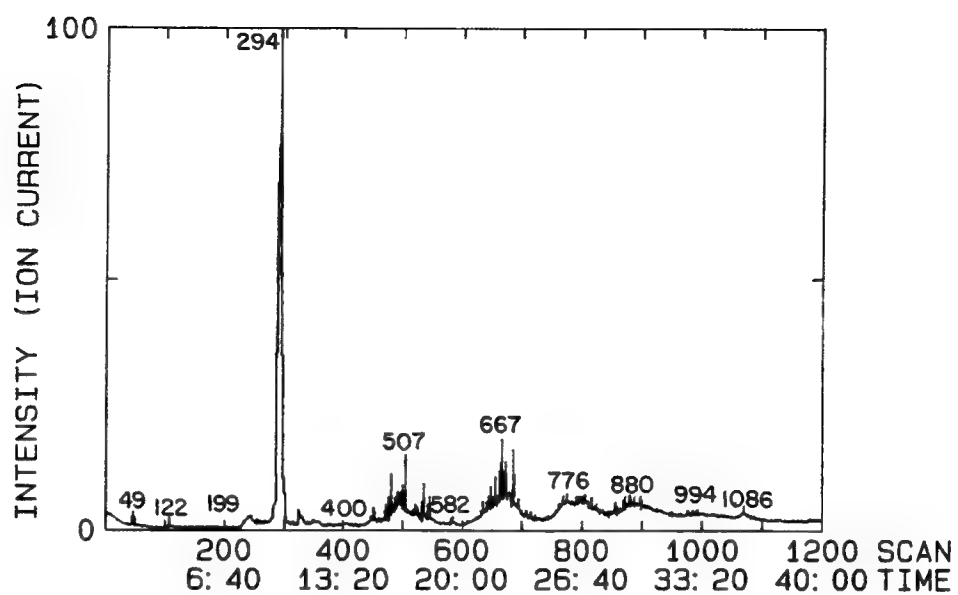


Figure 1a - Reconstructed ion chromatogram (RIC) of a sample of natural rubber following pyrolysis at 610°C.

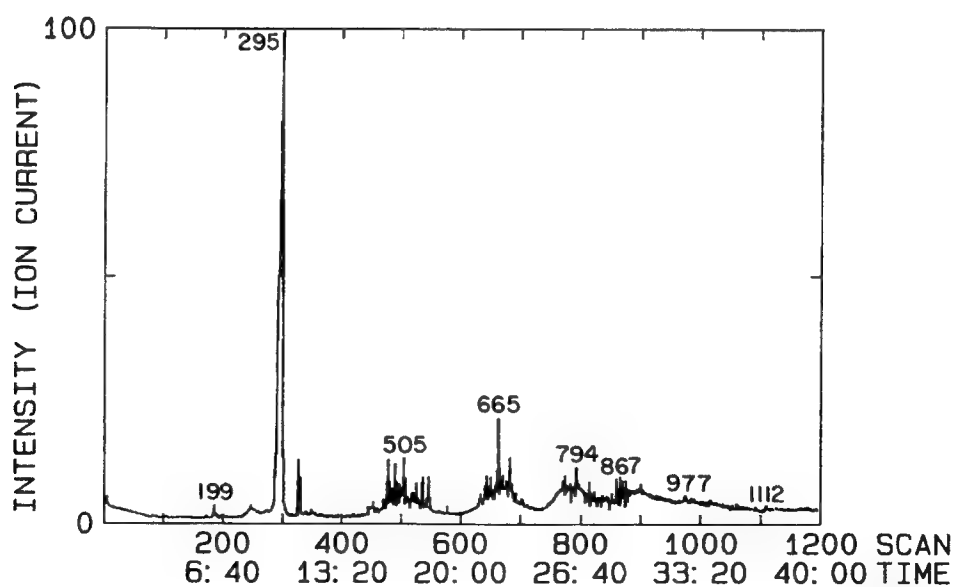


Figure 1b - Reconstructed ion chromatogram (RIC) of a sample of gamma radiation exposed natural rubber following pyrolysis at 610°C.

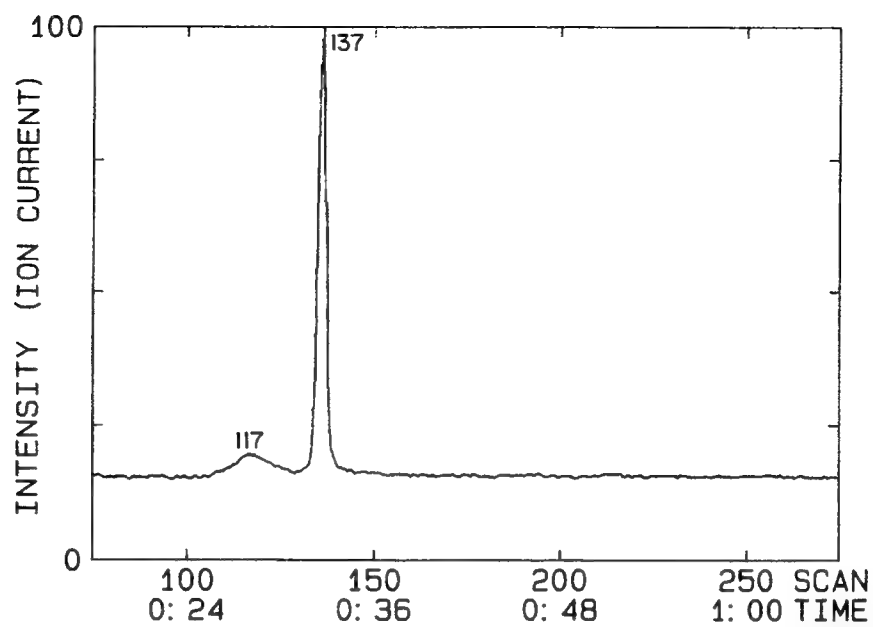


Figure 2a - Reconstructed ion chromatogram (RIC) of a sample of natural rubber following DEP analysis at 610°C.

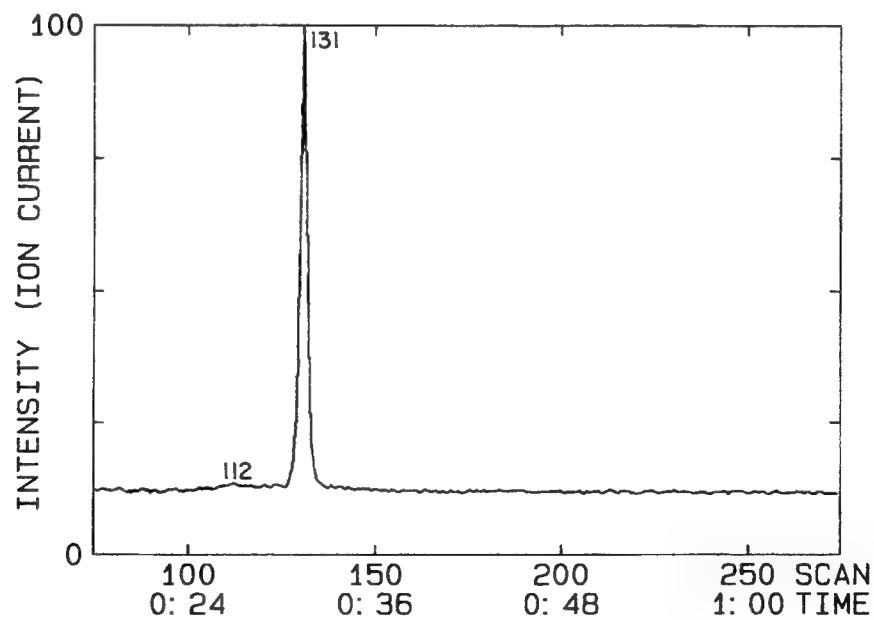


Figure 2b - Reconstructed ion chromatogram (RIC) of a sample of gamma radiation exposed natural rubber following DEP analysis at 610°C.

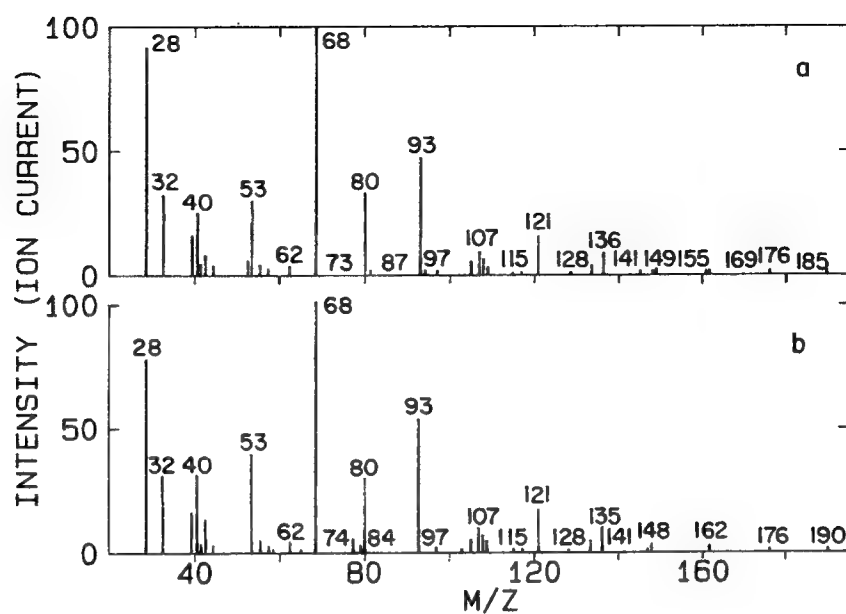


Figure 3 - Mass spectra of the major peak in the RICs of samples of a) natural rubber (scan 137) and b) gamma radiation exposed natural rubber (scan 131).

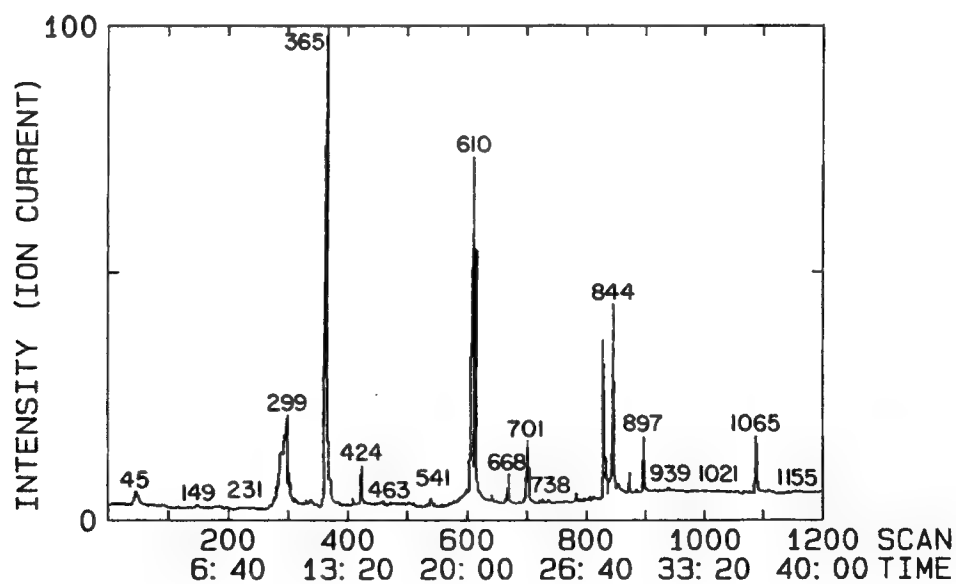


Figure 4a - RIC of a sample of polycaprolactone following py-GC/MS analysis at 610°C.

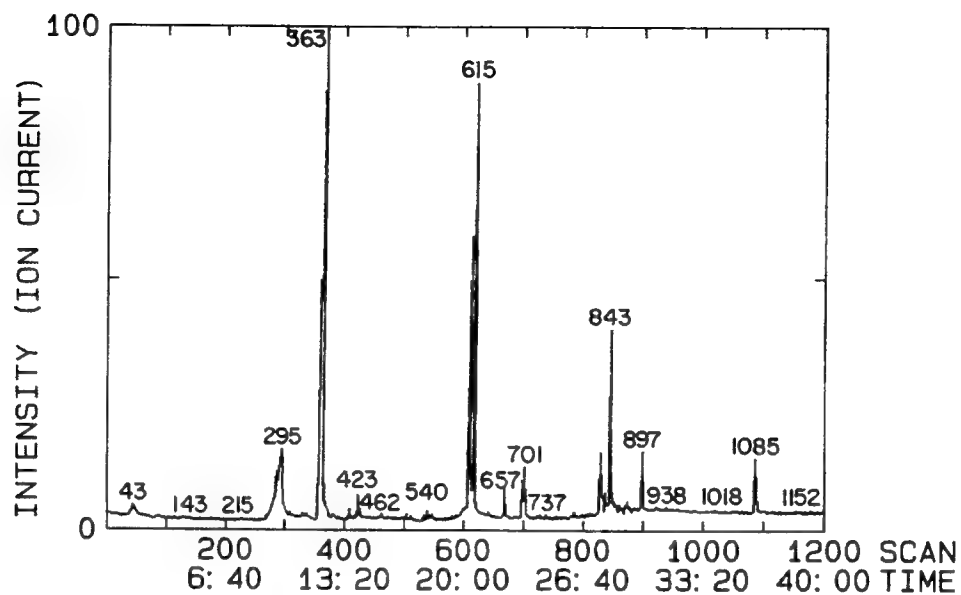


Figure 4b - RIC of a sample of gamma radiation exposed polycaprolactone following py-GC/MS analysis at 610°C.

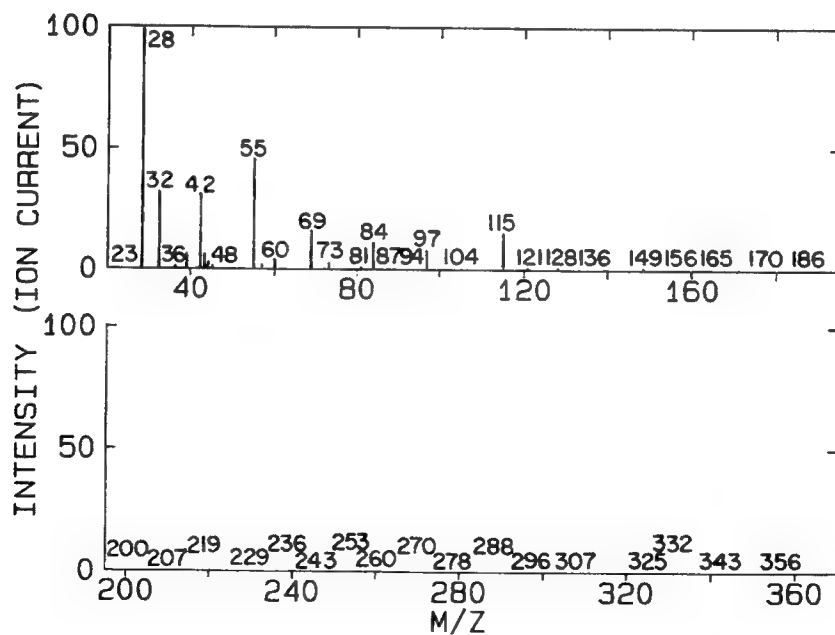


Figure 5a - Mass spectrum of a sample of PCL following DEP analysis at 610°C.

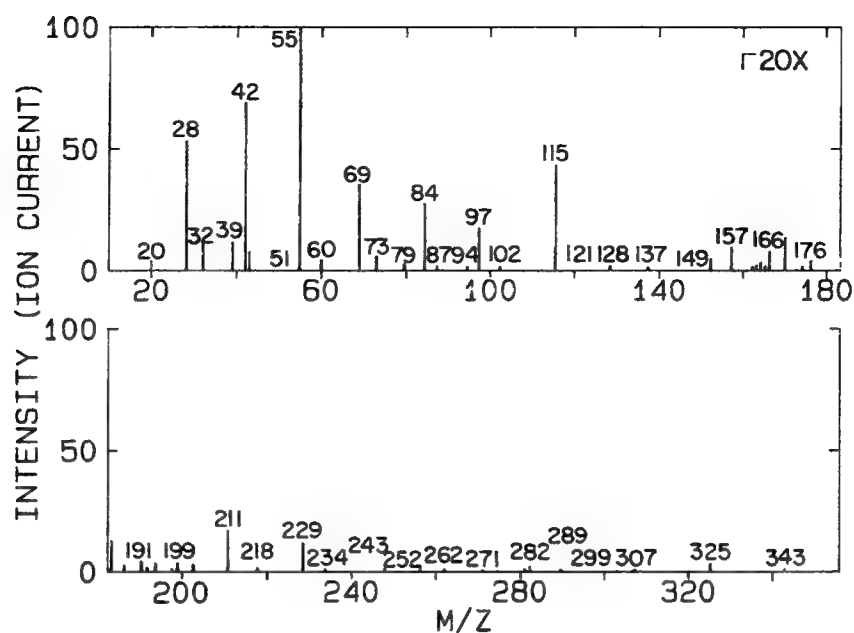


Figure 5b - Mass spectrum of a sample of gamma radiation exposed PCL following DEP analysis at 610°C.

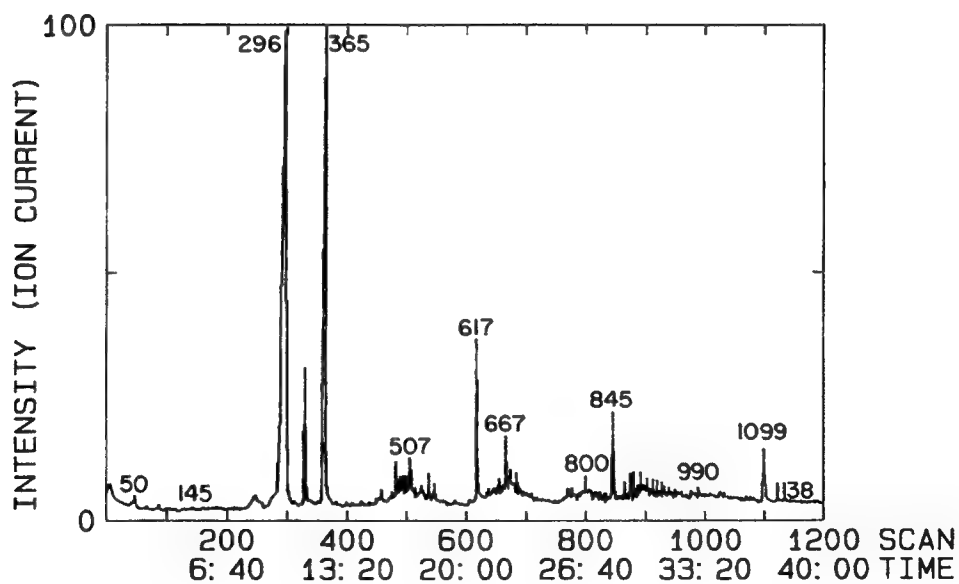


Figure 6a - RIC of a sample of mixture A following py-GC/MS analysis at 610°C

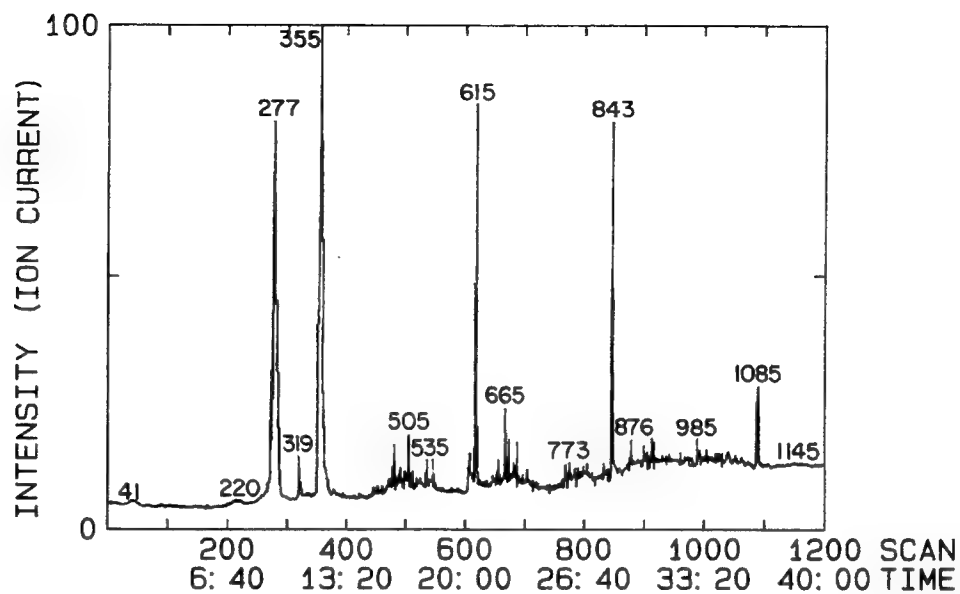


Figure 6b - RIC of a sample of gamma radiation exposed mixture A following py-GC/MS analysis at 610°C.

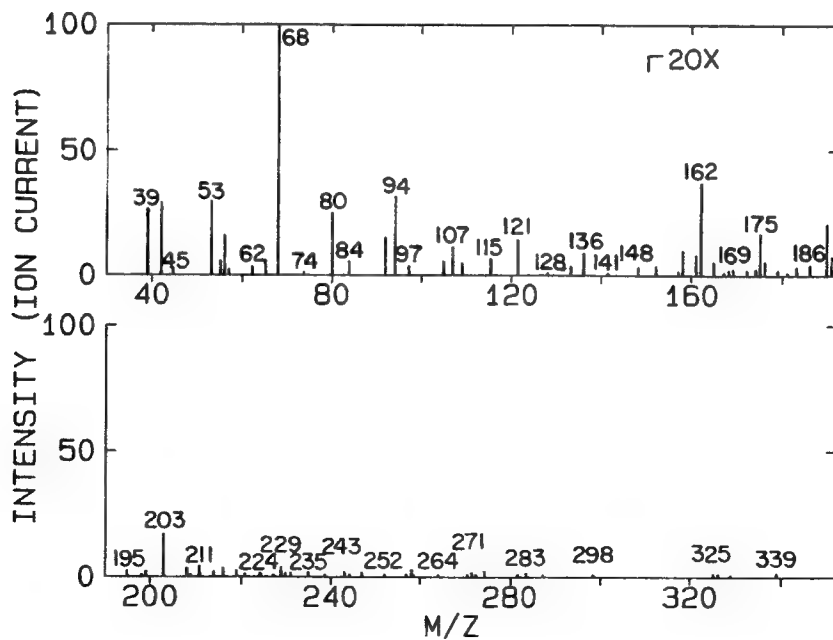


Figure 7a - Mass spectrum of a sample of mixture A following DEP analysis at 610°C.

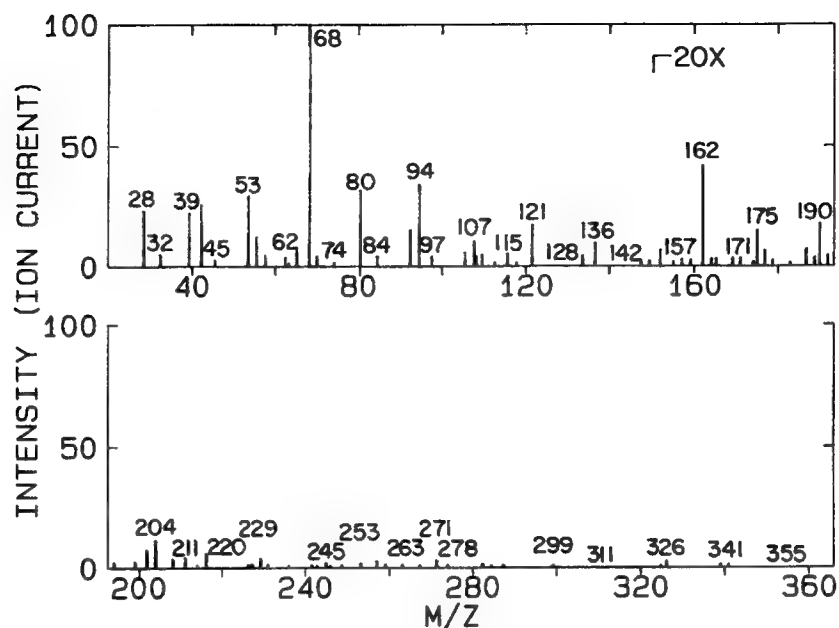


Figure 7b - Mass spectrum of a sample of gamma radiation exposed mixture A following DEP analysis at 610°C.

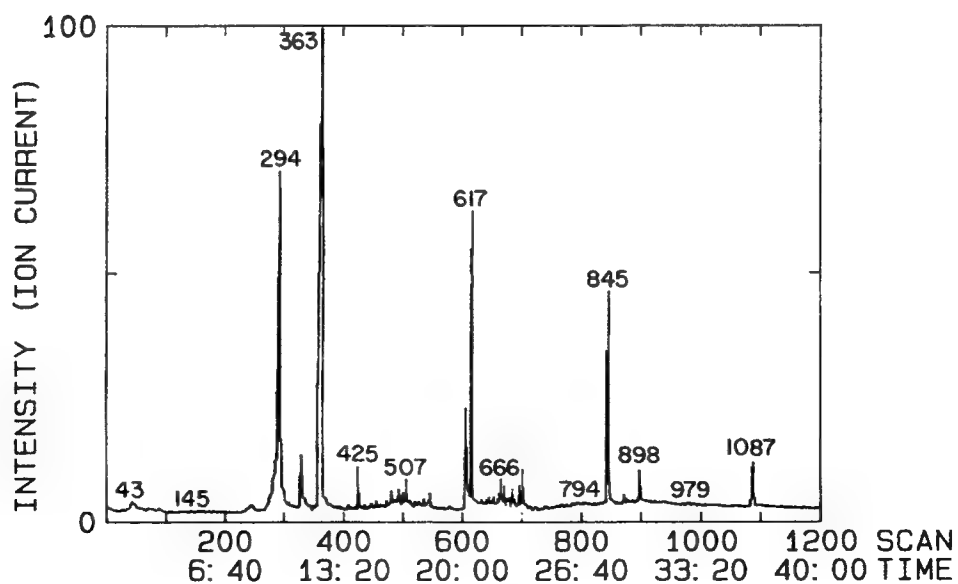


Figure 8a - RIC of a sample of mixture F following py-GC/MS analysis at 610°C.

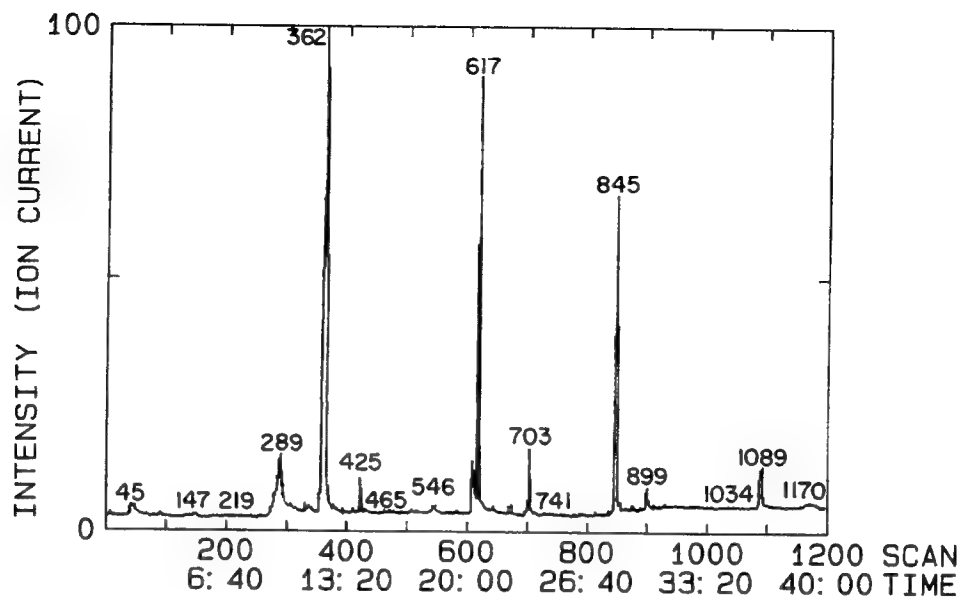


Figure 8b - RIC of a sample of gamma radiation exposed mixture F following py-GC/MS analysis at 610°C.

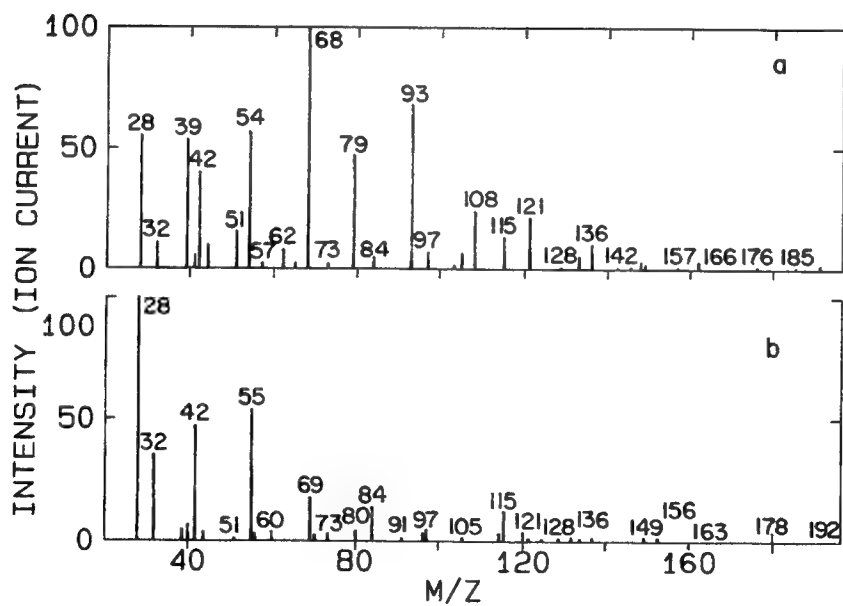
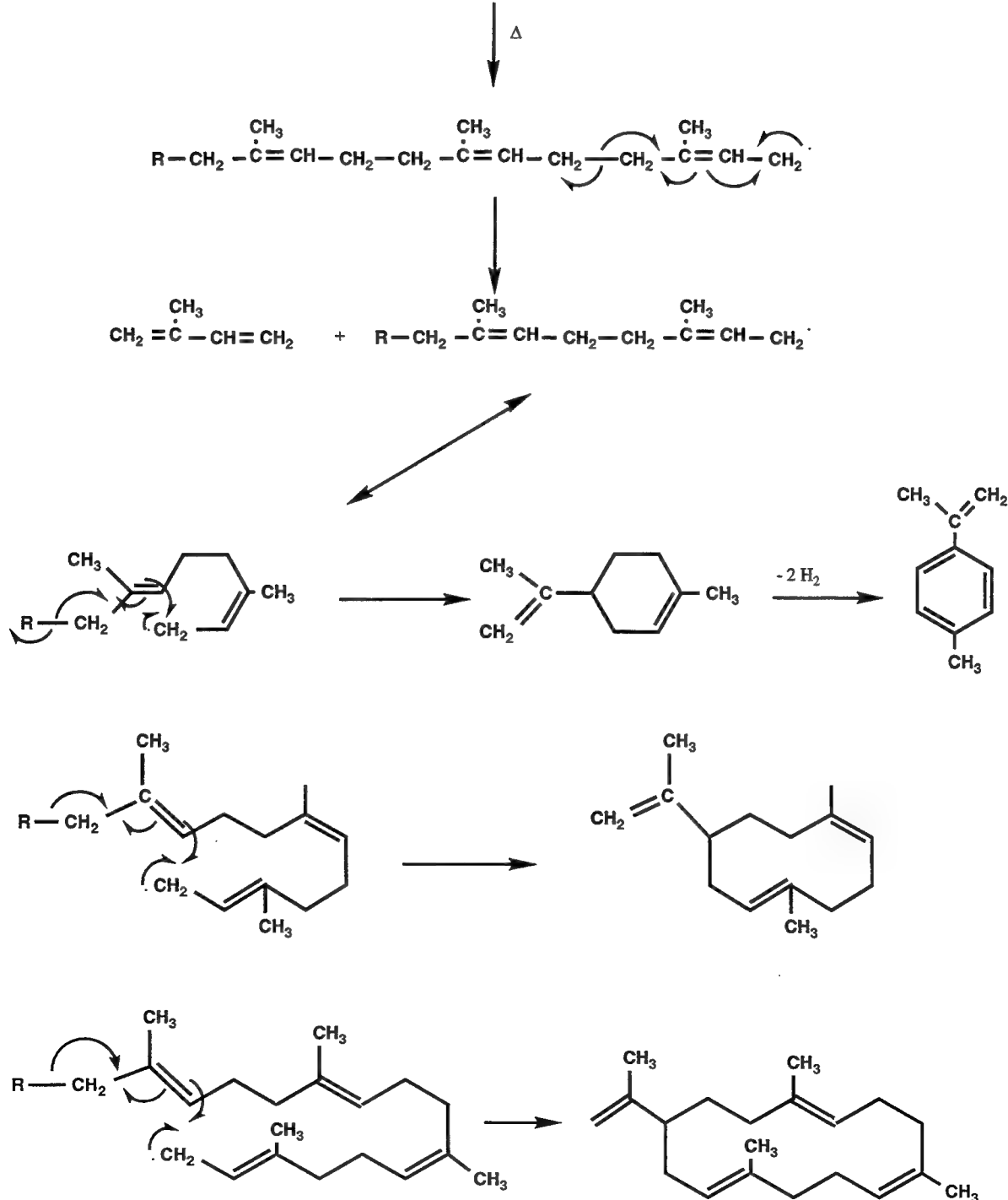
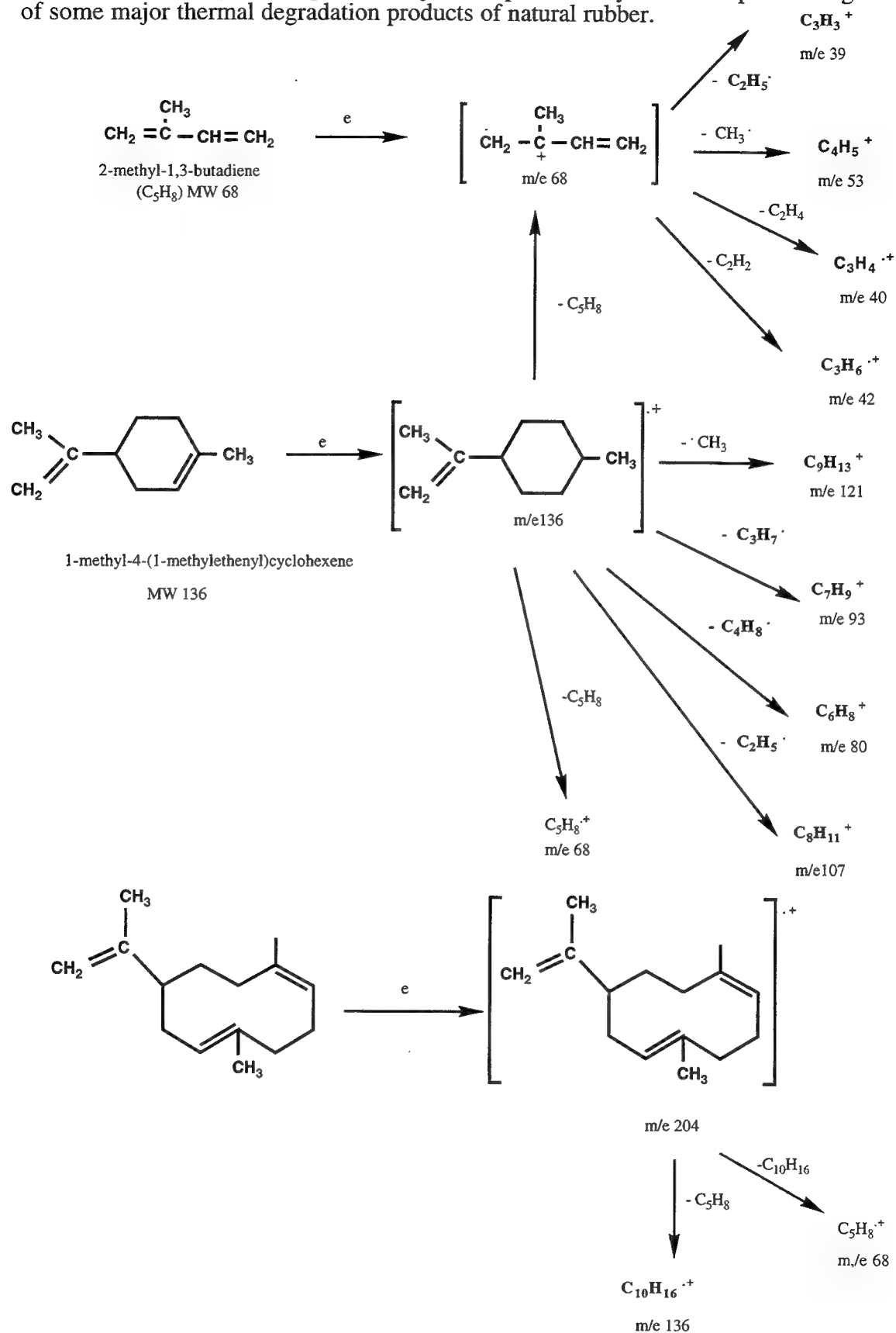


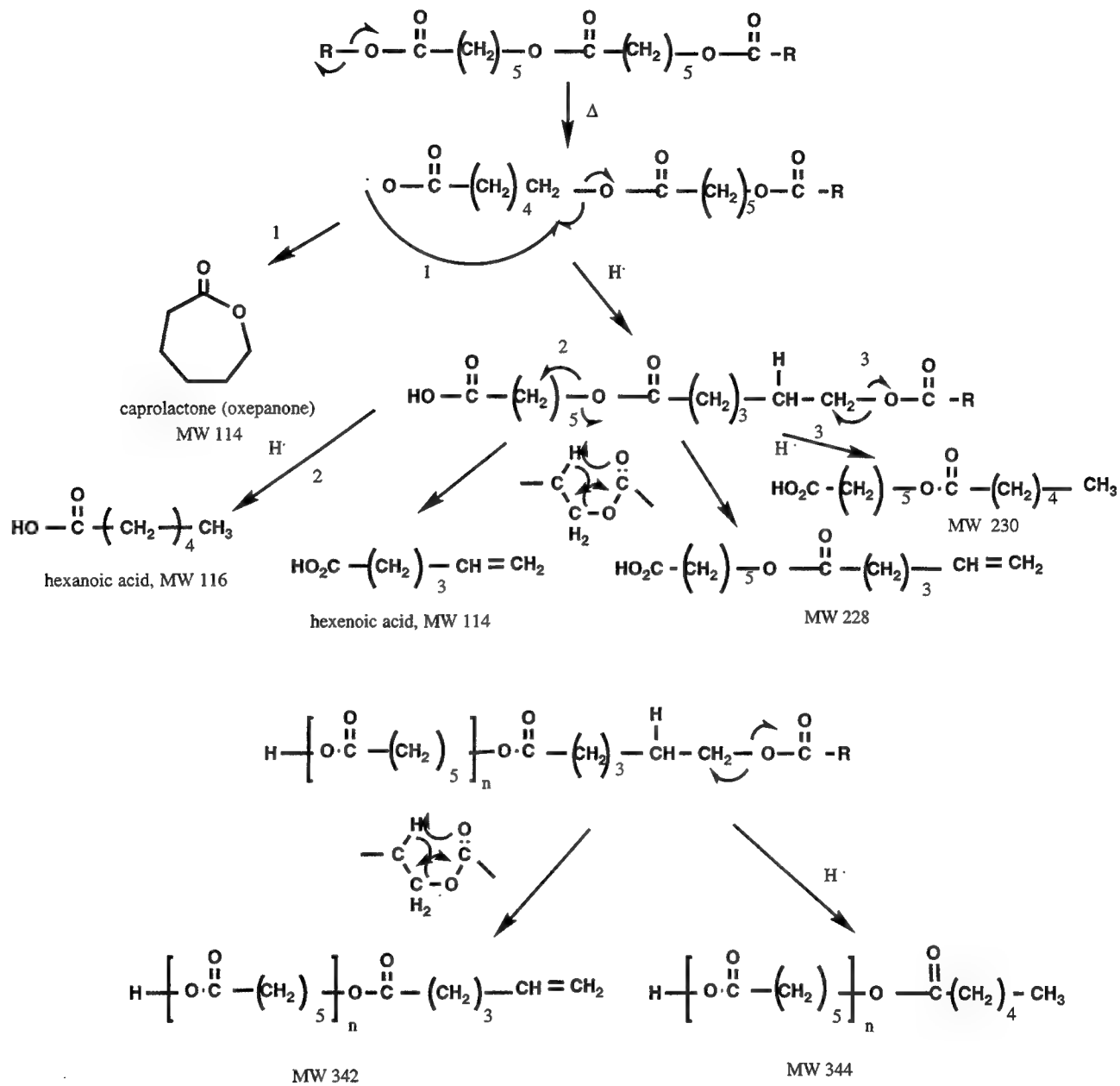
Figure 9 - Mass spectra of a) mixture F and b) gamma radiation exposed mixture F following DEP analysis.

$$\text{R}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\cdot}{\text{C}}}=\text{CH}-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{\cdot}{\text{C}}}=\text{CH}-\text{CH}_2-\text{CH}_2-\overset{\text{CH}_3}{\underset{\cdot}{\text{C}}}=\text{CH}-\text{CH}_2-\text{R}$$


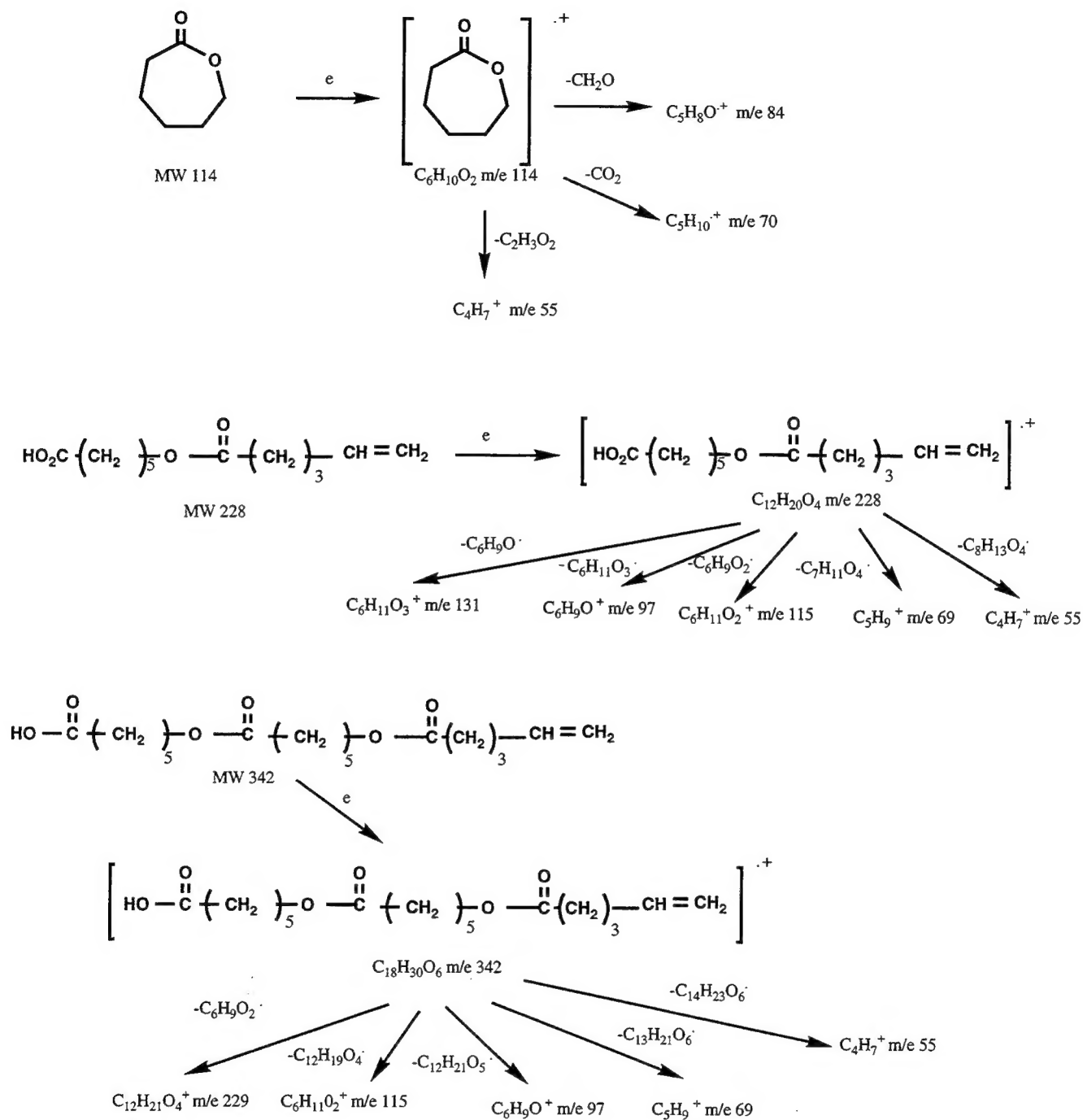
Scheme 2 - Pathways leading to the major ions produced by the mass spectral fragmentation of some major thermal degradation products of natural rubber.



Scheme 3 - Pathways leading to the formation of a number of the thermal degradation products of polycaprolactone.



Scheme 4 - Pathways leading to the major ions produced by the mass spectral fragmentation of the monomer, dimer, and trimer of caprolactone.



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This report describes the results of direct exposure probe-mass spectrometry and pyrolysis-gas chromatography/mass spectrometry studies of the effect of gamma radiation exposure on the thermal degradation products of natural rubber, polycaprolactone, 70 - 30 and 30 - 70 mixtures of natural rubber and polycaprolactone. The degradation products and their relative abundances of the natural rubber, polycaprolactone, and the 70 - 30 natural rubber - polycaprolactone mixture were similar before and after gamma radiation exposure. However, gamma radiation exposure did have an effect on the degradation products of the 30 - 70 natural rubber - polycaprolactone mixture. Prior to gamma radiation exposure, the degradation products of this mixture consisted of compounds characteristic of the two components of the mixture, while following gamma radiation exposure the degradation products were characteristic of the polycaprolactone portion of the mixture. Degradation products from the natural rubber portion of the mixture were not observed. Although this suggests that gamma radiation exposure changed the structure of the mixture, other techniques, such as sol gel analysis or molecular weight determination, are required to determine how the structure has changed.

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Polycaprolactone (PCL)
NR/PCL Blends
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Mass Spectrometry
Gamma Radiation
Degradation